

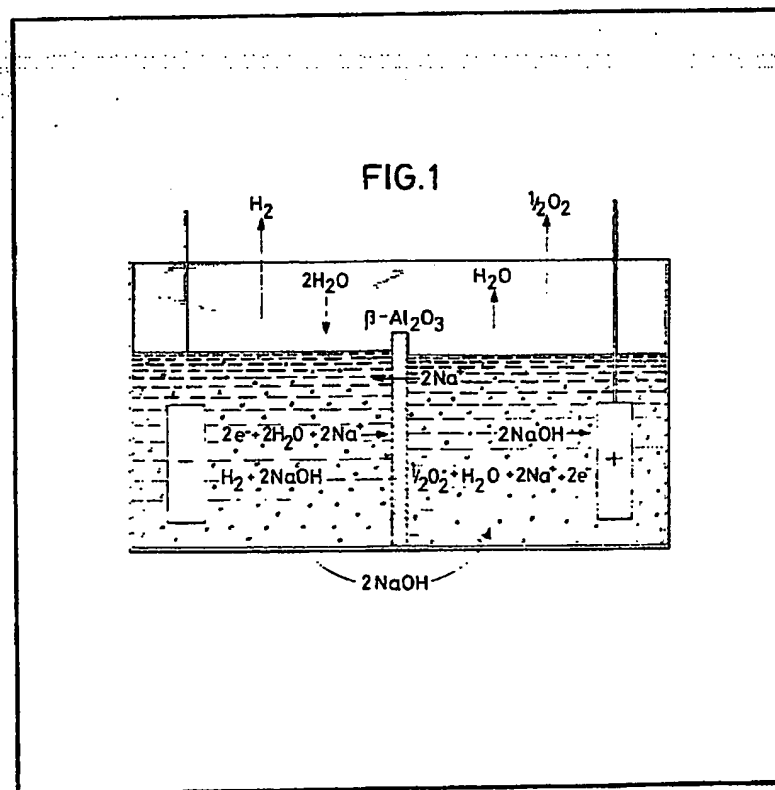
(12) UK Patent Application (19) GB (11) 2 010 333 A

- (21) Application No 7848977
 (22) Date of filing 18 Dec 1978
 (23) Claims filed 18 Dec 1978
 (30) Priority data
 (31) 2756569
 (32) 19 Dec 1977
 (33) Fed. Rep. of Germany (DE)
 (43) Application published
 27 Jun 1979
 (51) INT CL²
 C25B 1/10
 (52) Domestic classification
 C7B 146 215 235 265
 269 329 402 503 508 511
 514 517 554 758 769 D8
 DN
 (56) Documents cited
 GB 1491905
 (58) Field of search
 C7B
 H1B
 (71) Applicant
 Kernforschungsanlage
 Jülich, Gesellschaft Mit
 Beschränkter Haftung,
 Postfach 1913, 5170
 Jülich, Germany
 (72) Inventors
 Jiri Divisek,
 Jürgen Mergel
 (74) Agent
 Mewburn Ellis & Co.

(54) Process and Apparatus for the Production of Hydrogen and Oxygen

(57) In the electrolytic production of hydrogen and oxygen by electrolysis of molten alkali metal hydroxide, the

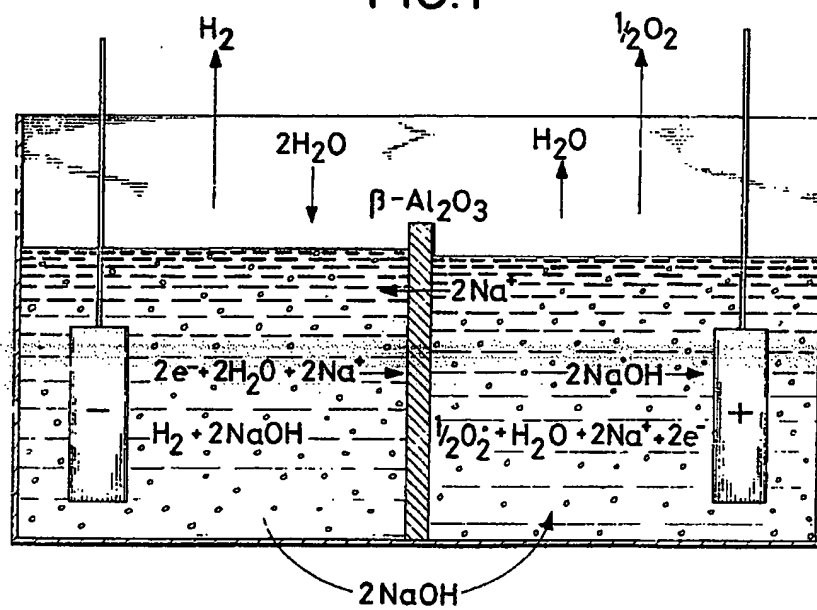
anode and cathode chambers are separated by means of a separator consisting of β - Al_2O_3 , which provides effective separation of the anode and cathode chambers and can withstand the hot alkali melt. A Ni anode and Ni or graphite cathode may be used.



UDELVUCC

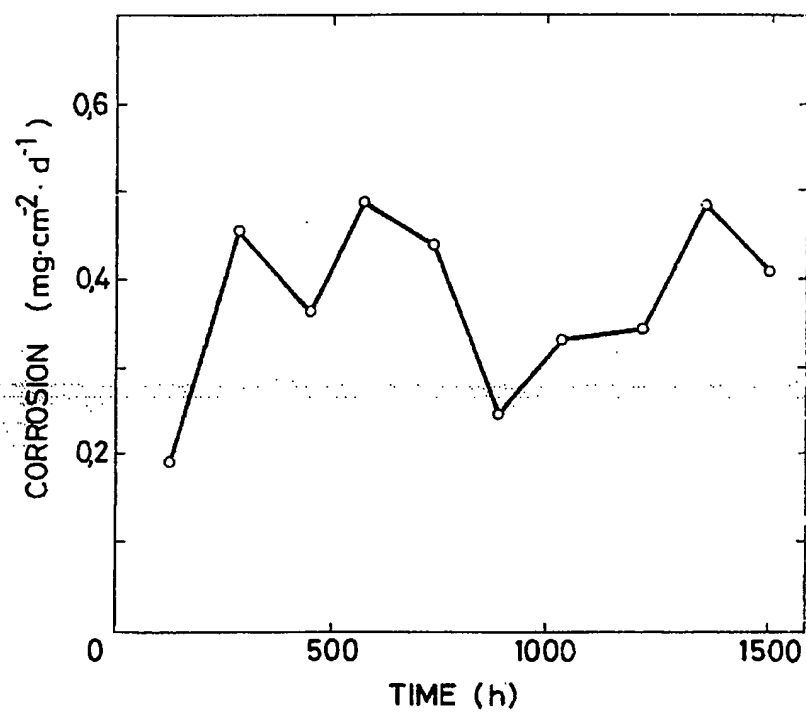
2010333

FIG. 1



2010333

FIG. 2



SPECIFICATION

Process and Apparatus for the Production of Hydrogen and Oxygen

The invention relates to a process for the
5 production of hydrogen and oxygen by electrolytic
decomposition of water in an electrolytic cell
containing a molten electrolyte which contains
alkali metal ions and has a high OH^- ion activity,
wherein hydrogen and oxygen are separately
10 withdrawn, and to an apparatus for carrying out
this process.

Increased attention is being devoted to the
production of hydrogen because hydrogen will
probably acquire great economic importance as a
15 future energy vehicle. Moreover, where thermal
energy must be supplied for this purpose, solar
energy and the energy produced in nuclear
reactors can be utilised.

The prior art includes a number of processes
20 for the production of hydrogen from water, most
of which, however, will not go beyond the
experimental stage.

The only hitherto-known process which has
been applied on an industrial scale is one in which
25 hydrogen and oxygen are produced by electrolysis
using as electrolyte an aqueous solution of
potassium hydroxide in a proportion of about 25%
by weight. The process is carried out at a
temperature between 70 and 90°C. In this
30 process, steel is used as the material for the
necessary electrolytic cell and for the cathode,
and nickel-coated iron is used for the anode.

However, this known process has the
disadvantage that the energy consumption is very
35 high. With a current density between 100 and
200 mA/cm^2 , the average energy consumption is
4.6 kWh/Nm^3 of H_2 and in the most favourable
case 4.2 kWh/Nm^3 of H_2 (see A. Schmidt
"Angewandte Elektrochemie [Applied
40 Electrochemistry]", Verlag Chemie, Weinheim,
1976, page 126).

Endeavours have already been made to lower
the energy consumption in the production of
hydrogen by carrying out the electrolysis under
45 elevated pressure, although the decomposition
voltage increases with increasing gas pressure.
However, an advantage of this is that the increase
in the voltage is cancelled out because the gas
bubbles formed in the electrolyte occupy a
50 substantially smaller volume owing to pressure
increase, so that the electrolyte resistance and
hence the cell voltage decreases (see A. Schmidt
"Angewandte Elektrochemie", Verlag Chemie,
Weinheim, 1976, page 127). Nevertheless, there
55 is the disadvantage that the cost of the apparatus
employed for the electrolysis is thereby
considerably increased.

The prior art also includes a process in which
pure water is decomposed with the use of a solid
60 electrolyte. In this case, there is employed as the
electrolyte sulphonated polytetrafluoroethylene
which is known by the abbreviation PTFE (see L.
J. Nutall, A. P. Fickett, W. A. Titterton,
"Hydrogen Generation by Solid Polymer

65 Electrolyte Water Electrolysis", Proc. Energy Conf.
Miami, 1974, page 9—33 to page 9—37). It is
true that this process has the advantage that it is
unnecessary to use a diaphragm for separating
hydrogen and oxygen, as was considered

70 desirable in the process known until then. It
also has the advantage that pure water can be
employed, so that corrosive influences are
eliminated. However, a considerable disadvantage
of this known process resides in the fact that

75 platinum must be used as the electrode material,
which substantially precludes application on an
industrial scale.

Owing to the unsatisfactory results of the
hitherto-known processes for the production of
80 hydrogen and oxygen, it has also already been
proposed, as a reversal of the procedure in
 $\text{H}_2\text{-O}_2$ fuel cells, to produce hydrogen and oxygen
with the use of a 25% potassium hydroxide
solution at a working temperature of 80°C. In this
85 case, an electrode made from hot-pressed
carbonyl nickel, produced by decomposition of
nickel carbonyl, was used as the highly porous
cathode.

The two electrolysis chambers necessary for
90 carrying out the electrolysis were separated by an
asbestos paper diaphragm (H. Ewe, "Chemie-
Ingenieur-Technik", MS 322/76). For improving
this process, it has also already been proposed to
make the cathode and in addition the anode of
95 Raney nickel, in order thereby to achieve
activation. Consequently, the cell voltage was
reduced by 20%. However, a disadvantage of this
is that the production of Raney nickel electrodes
is very costly. Apart from this, the expenditure of
100 energy necessary for carrying out this process is
still high.

The proposals for obtaining hydrogen and
oxygen in the most economical manner possible
also include a process in which the energy
105 liberated by a high-temperature reactor is utilised
for the production of a water vapour phase with a
temperature of about 1000°C and the water
vapour is split by means of a solid electrolyte. The
material employed for the electrolyte is ZrO_2 (see
110 W. Dönitz "Chemie-Ingenieur-Technik", MS
323/76, and W. Baukal, M. Döbrich, W. Kuhn
"Chemie-Ingenieur-Technik", 48th year, 1976,
No. 2, page 132). This process has the advantage
that considerable thermodynamic and kinetic
115 advantages are obtained from the use of a solid
electrolyte: the stabilised ZrO_2 used as electrolyte
in this process is at the same time a conductor of
oxygen ions. The electrolyte which is in contact
with porous electrodes on both sides
120 simultaneously separates the two gas chambers
from one another. However, a disadvantage
resides in the fact that, for carrying out the
process, the water vapour must be brought to a
temperature of at least 900°C, at which the solid
125 electrolyte has sufficient electrical conductivity.
Therefore, only at temperatures above 900°C
does an electrolytic decomposition take place.
Owing to these high temperatures which are
necessary for carrying out this process, the

possibility of application on an industrial scale is not yet apparent, or is in any case possible only to a limited extent.

The object of the invention is to provide a process, and apparatus for carrying out the process, by means of which it is made possible to obtain hydrogen and oxygen under economical conditions, so that the process can be applied on a large industrial scale. A particular aim is to reduce the necessary consumption of electrical energy as compared with the hitherto-known processes.

A method suitable in principle for achieving this object is an electrolytic decomposition of water which is passed as vapour into a melt containing OH^- , in particular into a melt containing alkali metal ions, as is already described in U.S. Patent Specification 1,543,357. However, the conditions indicated in this U.S. patent specification do not result in industrially useful production of hydrogen, and in particular the indicated separation of the anode chamber and cathode chamber by bells or a greater or lesser spatial distance does not permit a strict suppression of the diffusion of gases so that economic losses, which are no longer tolerable nowadays, are incurred by back-diffusion of gas. The considerable spatial separation, which is necessary in the known process, between the cathode and the anode has the consequence that unduly high voltage drops arise within the cell, and these virtually cancel out the competitiveness of the process. Moreover, the current efficiency is greatly reduced if peroxide compounds formed at the anode can pass without hindrance to the cathode, as is readily possible in the case of the U.S. patent specification. The resulting reductions in yield by about 10% are no longer acceptable economically.

A strict separation of the anode chamber from the cathode chamber should provide a remedy for this, but it is very difficult to find separators which are durable and can be used in the hot alkali melt. On the laboratory scale, corundum diaphragms are known, but these are completely unsuitable for industrial use on a relatively large scale since, on the one hand, they cause a very high resistance in the electrolytic cell, and, on the other hand, large-area separators are extremely difficult to manufacture.

It has now been found that an industrially satisfactory electrolytic decomposition of water is an electrolytic cell, containing a molten electrolyte, can be achieved in an elegant manner when the anode chamber is separated from the cathode chamber by a separator consisting of an aluminium oxide modification which is known as $\beta\text{-Al}_2\text{O}_3$ and is an ionic conductor.

According to one aspect of this invention there is provided a process for the production of hydrogen and oxygen by electrolytic decomposition of water in an electrolytic cell containing a molten electrolyte which contains alkali metal ions and has a substantial OH^- ion activity, wherein hydrogen and oxygen are

separately withdrawn, characterised in that the anode chamber is separated from the cathode chamber by a separator consisting of an aluminium oxide modification which is known as $\beta\text{-Al}_2\text{O}_3$ and is an ionic conductor.

Embodiments of this process can achieve a considerable reduction in the consumption of electrical energy as compared with the hitherto-known processes. In addition, embodiments of the process are suitable for performance at temperatures which render possible a supply of thermal energy in a relatively simple manner. The process can be carried out using materials for carrying out the reactions, such that there is no undue danger to the environment.

In a second aspect the invention provides an electrolytic cell for carrying out the process, having a nickel anode, nickel or graphite cathode.

The invention will be further explained with reference to the attached drawings in which, in particular:

Figure 1 is a diagrammatic representation of an electrolytic cell, illustrating the mode of action of the decomposition of water according to the invention, and

Figure 2 shows graphically the decrease in weight of a $\beta\text{-Al}_2\text{O}_3$ separator under operating conditions.

It can be seen from Figure 1 that the $\beta\text{-Al}_2\text{O}_3$ diaphragm merely allows alkali metal ions to pass through, whilst oxygen and hydrogen remain separate in the particular electrode chambers and can be withdrawn separately from the latter. To satisfy the mass balance, electrolyte is transferred from the cathode chamber into the anode chamber, and this can be effected in such a way that a carry-over of gases is impossible.

In addition to the advantage already mentioned that a complete separation of the gases is achieved, the separation, according to the invention, of the anode chamber from the cathode chamber by means of a $\beta\text{-Al}_2\text{O}_3$ separator has the advantage that the total cell voltage can be reduced since, according to the invention, electrode spacings are possible which merely correspond to the wall thickness of the separator, that is say they can amount to about 1 to 3 mm in practice. The electrical resistivity can here be even lower than that of the melt. Moreover, virtually 100% current efficiency is achieved according to the invention since a transfer of peroxide compounds formed at the anode into the cathode chamber is suppressed.

The electrolysis according to the invention is preferably carried out at temperatures of 300 to 600°C.

Suitable electrolytes are salts or salt mixtures which have a OH^- ion activity corresponding to an alkali metal hydroxide content of at least about 5% by weight and the melting point of which is below 800°C, in particular in the range from 300 to 600°C. Preferably, at least one of the salts is represented by an alkali metal hydroxide which, in particular, can be sodium hydroxide. Thus, sodium hydroxide alone or mixtures of sodium hydroxide

with other alkali metal hydroxides and/or alkali metal salts, in particular sodium salts, such as fluorides, sulphates or carbonates, are particularly suitable. The addition of lithium hydroxide which reduces the water content of the product gas and has an inhibitory action on the formation of peroxide is particularly advantageous. Potassium hydroxide appears to be less suitable.

A somewhat hygroscopic character of the electrolyte has the advantage that the release of undecomposed water vapour together with the product gases is reduced. Preferably, the electrolyte should thus contain a compound which is hygroscopic under the operating conditions.

The normal water content of the electrolyte melt will be in the region of about 0.5 to 4% by weight.

The β - Al_2O_3 separator provided according to the invention has a surprisingly high stability in melts of the abovementioned type, and it was possible to demonstrate this by corrosion tests extending over a prolonged period. The result is shown in Figure 2, which is a plot of corrosion in $\text{mg. cm}^{-2} \text{ day}^{-1}$ against operating time in hours. From this it can be seen that only a very slight corrosive consumption of the separator takes place, and this is virtually constant in time. The data were recorded in respect of operation at 410°C in molten sodium hydroxide containing 0.5% by weight of water.

A high OH^- ion activity of the electrolyte and the relatively high temperature at which the process is carried out are advantageous, in that electrochemical splitting of the water vapour is greatly favoured both thermodynamically and kinetically under these conditions. It may be desirable for the water vapour passed through or into the melt to be under a pressure above normal ambient pressure.

Nickel is very suitable as the material for the cathode and anode. It can, however, also be advantageous to use graphite as the material for the cathode and to use nickel as the material for the anode.

For supplying the water vapour in a particularly advantageous manner, the cathode may be constructed as a hollow body through which the water vapour is supplied.

The current density may be improved by making the cathode or the cathode and anode porous.

According to a preferred embodiment of the invention, porous electrodes can be brought into direct contact with the mutually opposite surfaces of the separator.

If sodium hydroxide is used as the salt melt, it has been found desirable to use nickel or nickel-coated iron as the material for the cell provided to receive the electrolyte.

Example 1

Water vapour under normal pressure was electrolysed in a NaOH melt at 430°C . The water vapour was introduced into the melt through a

porous graphite electrode which contained interstitial powdered activated charcoal (obtained by drawing a suspension of activated charcoal through under suction and subsequent drying). A nickel gauze was used as the anode. For

separating H_2 and O_2 , a ceramic diaphragm consisting of a solid β - Al_2O_3 electrolyte was provided. The partition had a resistivity of about $0.1 \Omega \text{ cm}$ at the operating temperature. This value is virtually negligible as compared with the electrical resistivity of the NaOH melt of about $0.45 \Omega \text{ cm}$. This was confirmed by an additional measurement which was made.

An α - Al_2O_3 crucible was used as the electrolytic cell. Alternatively, a nickel crucible may be employed. Hydrogen was evolved at the cathode, and oxygen was anodically formed. The nickel anode had become covered with a protective layer of nickel oxide; the corrosion of the anode was negligible during the experimental period, and a zero value was measured in practice.

For the removal of moisture, the NaOH melt had been dried before the electrolysis by passing argon (99.99%) through for three hours. The measured residual current density which corresponds to the residual moisture has a value of 10 mA/cm^2 at a cell voltage of 1250 mV and a value of 25 mA/cm^2 at a cell voltage of 1400 mV. After the introduction of water vapour, the measured current density had a value of 200 mA/cm^2 at a cell voltage of 1200 mV and reached a value of 400 mA/cm^2 at a cell voltage of 1400 mV. The decomposition potential of NaOH at the operating temperature of 430°C is 2.272 V.

Example 2

Water vapour under normal pressure was electrolysed in a NaOH melt at 400°C . Sheet nickel was employed as the electrode material both for the anode and for the cathode. The water vapour was introduced into the melt through a separate vapour duct in the neighbourhood of the cathode. The amounts of hydrogen and oxygen produced by the electrolysis were analysed by gas chromatography and the current efficiencies were calculated from these values. During the electrolysis which was initially carried out without separation of the two electrode chambers, the current efficiency was 90% of theory. Subsequently, an electrolysis was carried out under the same conditions with the same cell geometry, but with the electrode chambers separated by a β - Al_2O_3 separator. The current efficiency measured as before now reached 98 to 99% of theory.

A molar ratio, depending on the current density, of 20:1 ($\text{H}_2\text{O}:\text{H}_2$) was measured at 400 mA/cm^2 in the product gas from the electrolytic cell.

Example 3

Water vapour under normal pressure was electrolysed in a hydroxide melt of the composition $\text{NaOH}:\text{LiOH}=1:1$. The construction

and dimensions of the cell were not changed from those of Example 2. A molar ratio of $H_2O:H_2$ of 8:1 at a current density of 400 mA/cm² was measured in the product gas from the electrolytic cell. This means that the water content of the product gas was markedly reduced under the conditions of this example.

The current efficiency measured as in Example 2 was in this case virtually 100% of theory, that is to say it was yet further improved. To enable the improvement in current efficiency, which can be achieved by modifying the electrolyte, to be demonstrated even more clearly, the current efficiency was determined without a separator (under the same conditions). In this case, the efficiency was 96% as compared with 90% (which was obtained under the same conditions but using the electrolyte of Example 2). In this latter case, that is to say without the use of the separator, the separation of gas had of course deteriorated.

Claims

1. Process for the production of hydrogen and oxygen by electrolytic decomposition of water in an electrolytic cell containing a molten electrolyte which contains alkali metal ions and has a high OH^- ion activity, wherein hydrogen and oxygen are separately withdrawn, characterised in that the anode chamber is separated from the cathode chamber by a separator consisting of an aluminium oxide modification which is known as $\beta-Al_2O_3$ and is an ionic conductor.

2. Process according to claim 1, characterised in that the electrolyte contains a compound which is hygroscopic at the operating temperature.

3. Process according to claim 1 or claim 2, characterised in that the electrolyte contains a compound which is hygroscopic at the operating temperature.

4. Process according to any one of the preceding claims, characterised in that an alkali metal hydroxide or an alkali metal hydroxide

mixture, if desired together with alkali metal salts, is used as electrolyte.

5. Process according to claim 4 characterised in that sodium hydroxide is used as the alkali metal hydroxide.

6. Process according to claim 5 characterised in that a mixture of lithium hydroxide and sodium hydroxide is used as electrolyte.

7. Process according to any one of the preceding claims characterised in that water vapour is passed through or into the melt under a pressure above ambient pressure.

8. Process for the production of hydrogen and oxygen according to claim, substantially as described herein.

9. Electrolytic cell for carrying out the process of any one of the preceding claims, having a nickel anode, a nickel or graphite cathode, a $\beta-Al_2O_3$ separator separating the anode chamber of the cell from the cathode chamber, means for supplying water vapour to the electrolyte and means for separately withdrawing hydrogen and oxygen from the cathode chamber and anode chamber respectively.

10. Electrolytic cell according to claim 9, characterised in that the cathode is constructed as a hollow body for the supply therethrough of water vapour to the electrolyte.

11. Electrolytic cell according to claim 9 or claim 10 characterised in that either the cathode or both the anode and the cathode are porous.

12. Electrolytic cell according to any one of claims 9 to 11 wherein the electrodes are in contact with respective opposite faces of the separator.

13. Electrolytic cell according to any one of claims 9 to 12, characterised by a receiver vessel for the electrolyte, which vessel consists of nickel, nickel-coated iron or α -alumina.

14. Electrolytic cell according to claim 9 and substantially as herein described with reference to the drawings.